

Preface

Bilayers formed by molecules that possess long alkyl hydrophobic tails are ubiquitous in the natural world manifesting both in biological systems as well as in chemistry. The lipid bilayer is an integral feature of cell membranes of living systems with functions that are of critical importance to the life of the cell. Long chain amphiphilic surfactant molecules can be introduced within the interlamellar region of layered inorganic host lattices to form anchored alkyl chain bilayers within the galleries. The intercalated bilayer bears a striking resemblance to lipid bilayers. However, unlike lipid bilayers where individual molecules can undergo lateral diffusion and also flip-flop between layers the anchored bilayer is characterized by the total absence of translational mobility. The degrees of freedom of the alkyl chains of the anchored bilayer are restricted to changes in conformation.

This thesis describes a detailed investigation of the anchored bilayer formed by the intercalation of the anionic surfactant dodecyl sulphate (DDS) in a layered solid, Mg-Al Layered Double Hydroxide (Mg-Al LDH) using both experimental measurements and Molecular Dynamics (MD) simulations (**Chapter 2**). The thesis is organized as two parts. The first (**Chapters 2 - 4**) deals with the anchored bilayer in the condensed phase - the conditions for the formation of the bilayer arrangement of the intercalated surfactant chains and the conformation and dynamics of the alkyl chains of the surfactant in the galleries of the layered solid. The surfactant intercalated Mg-Al LDH-DDS may be delaminated in nonpolar solvents to give colloidal dispersions of individual Mg-Al LDH sheets with the DDS surfactant chains remaining tethered to the inorganic sheets (Scheme 1). The second part of thesis (**Chapters 5 - 9**) describe studies on the dispersions of the Mg-Al LDH-DDS in toluene.

A summary of the results of the of the investigations of the anchored bilayer, formed by the intercalation of DDS ions in Mg-Al LDH, in the condensed and the dispersed phases is presented in the concluding chapter (**Chapter 10**).

Layered Double Hydroxides (LDH) are insulating lamellar solids of the general chemical formula $[M'_{(1-x)}M_x(OH)_2]$, where M' is a divalent metal ion and M a trivalent ion. Their structure may be derived from that of Brucite, $Mg(OH)_2$, by isomorphous substitution of a part of the Mg^{2+} by trivalent ions like Al^{3+} with electrical neutrality maintained by interlamellar exchangeable ions. The studies reported in this thesis are on an Mg-Al LDH, $Mg_{(1-x)}Al_x(OH)_2$, x ranging from 0.17 to 0.37. Dodecyl sulphate surfactant ions have been ion-exchange intercalated in Mg-Al LDH (**Chapter 3**). By varying the Mg-Al ratio, differing packing densities of the surfactant chains in the interlamellar space of the Mg-Al LDH-DDS are realized. At high packing densities the alkyl chains of the intercalated dodecyl sulphate ions anchored on opposing Mg-Al LDH sheets are arranged as bilayers while at lower packing densities the surfactant chains form a monolayer with the chains oriented flat in the galleries. This composition driven monolayer to bilayer transformation in the surfactant intercalated Mg-Al LDH-DDS is also reproduced by MD simulations. The simulations also indicate that there are profound differences in the factors that decide the arrangement of the surfactant chains. In the bilayer arrangement it is dispersive van der Waals interactions between the chains in opposing layers that is responsible for the cohesive energy of the solid whereas at lower packing densities, where a monolayer arrangement is favored, Coulomb interactions between the positively charged Mg-Al LDH sheets and the negatively charged head-group of the DDS anion dominate.

The conformation and dynamics of the alkyl chains of the intercalated surfactant chains in both the monolayer and bilayer arrangements as well as the effect of packing density on these parameters is reported in **Chapter 4**. The conformation was studied using spectroscopic techniques, infra-red, Raman and ^{13}C Nuclear Magnetic Resonance (NMR) while the dynamics by Variable Contact Time Cross Polarization Magic Angle Spinning (VCT - CPMAS) and 2D Wideline Separation (2D WiSe) NMR techniques. The results showed the expected trends; the concentration of *gauche* defects and the dynamics of the chains increase with decreasing packing density. There is, however a sharp increase in the *gauche* concentration and conformational mobilities of the intercalated surfactant chains associated with the bilayer to monolayer transformation. The results of the MD simulations, too, reflect these trends.

The second part of thesis describes the delamination of the intercalated anchored bilayer (Mg-Al LDH-DDS) in non-polar solvents. Delamination results in a colloidal dis-

persion of the anchored bilayer, isolated Mg-Al LDH sheets with the DDS chains tethered to them, as neutral nanosheets of nanometer thickness and micron size. With increasing concentration of the anchored bilayers in the solvent a gel state is realized. The sol to gel transformation of the dispersions of the anchored bilayer in toluene has been investigated. Frequency dependent rheology measurements (**Chapter 6**) were used to investigate the visco-elastic properties of the dispersions and Small Angle X-ray Scattering (SAXS) measurements (**Chapter 7**) to understand the structure and shape of the nanosheets. The rheology experiments showed that the dispersions irrespective of their concentrations showed shear thinning. The SAXS results indicate a tactoid structure of the dispersions as well as in the gel phase. At higher concentrations, the X-ray scattering curves indicated that the layers stack loosely with an interlamellar space of ~ 39 Å, a value much larger than the interlayer lattice spacing of solid Mg-Al LDH-DDS (~ 27 Å).

The nature of interactions between solvent molecules and the anchored DDS chains were probed by ^1H and ^2H NMR measurements (**Chapter 8**). A clear association between the toluene molecules and the alkyl chains of the anchored surfactant was observed. $2D$ NOESY experiments established that there are toluene molecules in close proximity that interact with the methyl tail of the anchored surfactant. NMR measurements were also able to distinguish two types of solvent molecules based on their widely differing mobilities. MD simulations (**Chapter 9**) of the dispersed anchored bilayer are able to reproduce the essential features of the experimental observations including the formation of a loosely bound lamellar structure. It also provides an explanation on how the spectroscopic observation of motional heterogeneity gives rise to the viscoelastic properties of the dispersed anchored bilayer.